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(54) **Non-aqueous electrolyte secondary battery**

Sekundärbatterie mit nichtwässrigem Elektrolyten

Batterie secondaire à électrolyte non-aqueux

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- **PATENT ABSTRACTS OF JAPAN** vol. 17, no. 178 (E-1347) & JP-A-04 332479 (SONY CORP)
- **PATENT ABSTRACTS OF JAPAN** vol. 14, no. 502 (E-0997) & JP-A-02 207464 (SHOWA DENKO KK)
- **PATENT ABSTRACTS OF JAPAN** vol. 94, no. 012 & JP-A-06 338347 (SONY CORP), 6 December 1994,

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DescriptionBACKGROUND OF THE INVENTION5 Field of the Invention

[0001] The present invention relates to a non-aqueous electrolyte secondary battery for obtaining electromotive force due to introduction and discharge of lithium ions, and more particularly to a technique for preventing overcharge of the battery due to chemical reactions of additives.

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Prior Art

[0002] Security is the most important consideration for a lithium secondary battery (non-aqueous electrolyte secondary battery). In particular, protection from overcharge is an important fact.

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[0003] For example, if the charge voltage for, for example, a nickel-cadmium battery, has been raised, consumption of charge energy taking place due to chemical reactions of water which causes an overcharge protective mechanism to act. However, for the lithium secondary battery, which is a non-aqueous type secondary battery, another mechanism must be found.

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[0004] As an overcharge protective mechanism for the lithium secondary battery, there have been suggested a method using an electronic circuit, a method of mechanically interrupting an electric current by using gas generation when overcharge takes place, a shut down method using fusion of a separator and a method using chemical reactions of a reagent. However, each method has the following problem and, therefore, a satisfactory overcharge protective mechanism has not been realized yet.

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[0005] The method using an electronic circuit or the method of mechanically interrupting an electric current causes the battery to have an additional structure. Therefore, the cost of the battery cannot be reduced and various limitations arise in designing a product of the battery.

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[0006] The shut down method using fusion of a separator is a method using rise in the temperature of the battery when overcharge has taken place to fuse the separator with heat to close (shut down) a multiplicity of small apertures formed in the separator so as to interrupt the overcharge electric current. In the foregoing case, the separator is made of material which can relatively easily be fused.

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[0007] Heat which raises the temperature of the battery is considered to be generated due to reactions of lithium of the negative pole deposited due to overcharge and metal oxides of the positive pole made unstable because lithium ions have been excessively drawn due to overcharge and the electrolyte. Since the foregoing heat generation takes place considerably rapidly, heat generation cannot be interrupted even after the separator has been shut down and, thus, the overcharge electric current has been interrupted. Therefore, the temperature of the battery is frequently raised excessively and thus a problem of thermal runaway arises. As a result, in practical batteries, the shut-down type separator has not been used to prevent overcharge but the same has been employed to prevent short circuit occurring with the outside of the battery.

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[0008] Accordingly, another method has been energetically researched and developed which uses chemical reactions to prevent overcharge. For example, a method has been attempted in which an appropriate oxidation-reduction reagent is added to the electrolyte. In a case where the reversibility of the oxidation-reduction reagent is excellent, a protective mechanism is realized in which the reagent reciprocates between the positive pole and the negative pole to consume the overcharge electric current.

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[0009] The foregoing oxidation-reduction reagent is called a "redox shuttle" or the like. Simplification of the safety apparatus of the lithium secondary battery by using the redox shuttle realizes advantages in that the cost can be reduced and lowering of the battery energy density occurring due to the safety apparatus can be prevented as compared with the electronic circuit method. As for possibility in applying the redox shuttle to the lithium secondary battery, a fact that application of ferrocene is advantageous in a case where the battery is a 3 V type battery has been suggested in, for example, Japanese Patent Application Laid-Open publication No. 1-206571(1989).

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[0010] However, since the oxidation-reduction potential of the ferrocene with respect to lithium is 3.1 V to 3.5 V, it cannot be adapted to a battery having higher battery voltage. For example, a carbon-LiCoO₂-type lithium ion battery, which is a 4-V class battery, must employ a compound having an oxidation-reduction potential of about 4.0 V to about 4.5 V.

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[0011] Further improvements resulted in a disclosure in Japanese Patent Application Laid-Open publication No. 6-338347 (1994) in which metal complexes, such as Fe (5-Cl-1, 10-phenanthroline)₃X₂ and Ru (phenanthroline)₃X₂ (where X is an anionic molecule), and cerium salts, such as Ce (HN₄)₂(NO₃)₅, have been suggested as oxidation-reduction reagents adaptable to the 4-V-class lithium ion secondary battery. Transition metals, such as Fe, Ru and Ce, which are the central metals of the oxidation-reduction reagents, have a plurality of stable oxidation-reduction states

due to states of d-orbital or f-orbital. By coordinating appropriate ligands or by forming the same into solvated molecules, the oxidation-reduction potential can be controlled so that the foregoing transition metals are employed as preferred redox shuttles for the 4-V-class battery.

[0012] However, since each of the foregoing metal complexes and cerium salts has a structure such that large group of atoms surrounds the orbits of the central metals, they have large volume per molecular weight or per molecule. Therefore, the concentration and diffusion rate of the reagent molecules in the electrolyte are limited. Thus, there frequently arises a problem in that the effect of preventing overcharge cannot be obtained satisfactorily.

[0013] As another redox shuttle adaptable to the 4-V class battery, a compound has been disclosed in Japanese Patent Application Laid-open publication No. 7-302614(1995) in which an electron donative substitutional group, such as an alkyl group or a methoxy group, is induced into a benzene ring. Since the foregoing compound has a small molecular weight and a small volume per molecule as compared with those of the metal complex and cerium salt, satisfactory solubility and operations to serve as a redox shuttle can be obtained.

[0014] However, since the redox shuttle has a theoretical limiting current, a satisfactory effect of preventing overcharge cannot be obtained if the overcharge electric current is greater than a predetermined value. Specifically, the limiting current of each of the redox shuttles, which have been suggested, is not sufficiently large with respect to overcharge occurring in a case where charge has been performed at a rate (current capacity/charge period) of 1, that is, charge has been performed with a constant current of 1C (Ah/h) or greater.

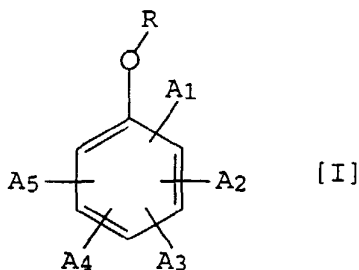
[0015] To prevent overcharge occurring with a great current, the foregoing method using an electronic circuit or the method of mechanically interrupting the electric current using generation of gas if overcharge takes place is relatively effective. Therefore, in a case where the redox shuttle is employed in a battery system in which charge is performed with a great electric current, the foregoing method must also be employed.

[0016] The addition of aromatic compounds, optionally having alkyl, alkoxy and/or halogen substituents, as corrosion-protective agents to the organic solvent of lithium secondary batteries is disclosed in DE-A-28 34 485. Said corrosion-protective agents are selected such that they do not chemically react with the electrode and are not chemically modified during use of the battery.

OBJECT AND SUMMARY OF THE INVENTION

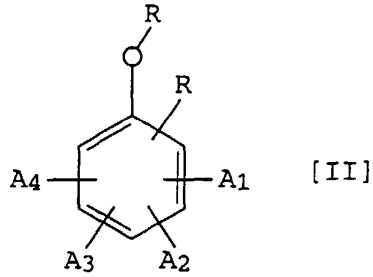
[0017] In view of the foregoing, an object of the present invention is to provide a non-aqueous electrolyte secondary battery having a reagent satisfactorily serving as a mechanism of preventing overcharge even adapted to a 4-V-class battery which is charged with a great electric current and exhibiting high energy density and satisfactory safety and low cost.

[0018] To achieve the foregoing object, according to one aspect of the present invention, there is provided a non-aqueous electrolyte secondary battery according to claim 1. The battery comprises a negative pole made of metal material mainly composed of lithium or carbon material capable of doping and removing lithium; a positive pole made of a composite oxide of lithium and transition metal; and an electrolyte which is a non-aqueous electrolyte in which a support salt is dissolved in a non-aqueous solvent, wherein the non-aqueous electrolyte contains a benzene compound having a small molecular weight, e.g., a molecular weight of 500 or less, more preferably 200 or less, and a reversible oxidation-reduction potential at a potential higher than the potential at the positive pole in a state where the non-aqueous electrolyte secondary battery is fully charged and having a p-electron orbital. The benzene compound is selected from the group consisting of compounds expressed by General Formulas [I] to [V]:



where R is an alkyl group, A₁, A₂, A₃, A₄ and A₅ are each H or halogen and at least any one of A₁, A₂, A₃, A₄ and A₅ is halogen;

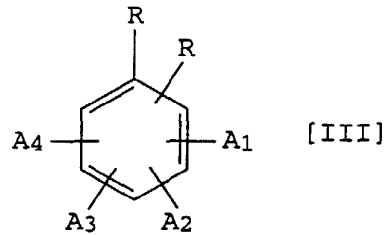
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where R is an alkyl group, A₁, A₂, A₃ and A₄ are each H or halogen and at least any one of A₁, A₂, A₃ and A₄ is halogen;

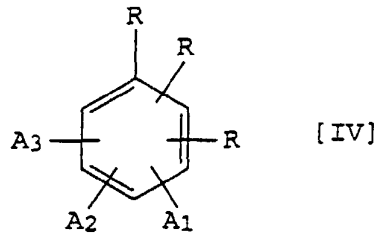
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where R is an alkyl group, A₁, A₂, A₃ and A₄ are each H or halogen and at least any one of A₁, A₂, A₃ and A₄ is halogen;

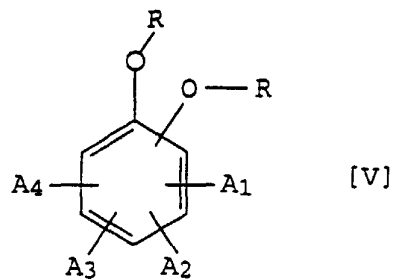
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where R is an alkyl group, A₁, A₂ and A₃ are each H or halogen and at least any one of A₁, A₂ and A₃ is halogen;

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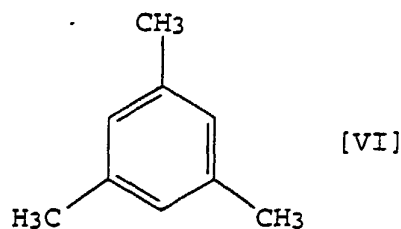
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Where R is an alkyl group, A₁, A₂, A₃ and A₄ are each halogen.

[0019] According to another embodiment of the invention, there is provided a non-aqueous electrolyte secondary battery according to claim 3. In this embodiment, the support electrolyte is LiBF₄ and the benzene compound is expressed by Formula VI:

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10 [0020] It is preferable that the non-aqueous electrolyte secondary battery containing the benzene compound in the non-aqueous electrolyte thereof employs a polyolefin porous film which is, as a separator, disposed between the positive pole and the negative pole.

15 [0021] Other objects, features and advantages of the invention will be evident from the following detailed description of the preferred embodiments described in conjunction with the attached drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

[0022]

20 Fig. 1 is a vertical cross sectional view showing an example of the structure of a non-aqueous electrolyte secondary battery according to the present invention;

Fig. 2 is a schematic view showing a measurement circuit system for use in performing a constant electric current overcharge test of the non-aqueous electrolyte secondary battery; and

25 Fig. 3 is a graph showing the terminal voltage when the battery has been overcharged and change in the temperature of the battery as the time passes of a battery in which 2-chloro-p-xylene is added to the electrolyte thereof and a battery to which no 2-chloro-p-xylene is added to the electrolyte thereof.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

30 [0023] Each of the foregoing benzene compounds acts as a mechanism for preventing overcharge. The mechanism for preventing overcharge is realized due to chemical reactions such that the benzene compound performs an oxidation-reduction reaction if the battery has been overcharged, and then the oxidized compounds continuously are dimerized to polymerized or adsorbed to the activated electrode or react with the same. The mechanism for preventing overcharge will now be described.

[0024] The benzene compound has an effect to serve as the redox shuttle, that is, an effect of consuming the overcharge current by the oxidation-reduction reactions.

35 [0025] The foregoing effect can be obtained because the benzene compound has an appropriate oxidation-reduction potential as the redox shuttle for a 4-V-class battery and is able to chemically stabilize oxidation species and reduction species by selecting a substitutional group.

40 [0026] That is, a covalent bond of two atoms of an organic compound, in principle, is such that two electrons forming a pair form one single bond. Therefore, when an organic compound is oxidized or reduced to remove or add one electron from an electron system of the bond of the organic compound, an unpaired electron is formed in the organic molecule compound. Although the unpaired electron can be stabilized when decomposition of the organic compound has been resulted in a novel bond with another molecule being formed, the state of the organic compound having the unpaired electron is instable in principle.

45 [0027] However, in a case where unpaired electrons exist on a delocalized orbit and spread over two or more atoms in a molecule as can be observed in a p-orbital of an aromatic series, the organic compound is able to relatively stably exist even if the organic compound has unpaired electrons. If the reaction active point at which the density of the unpaired electrons is high is protected from attacks of other molecules due to a steric hindrance of the substitutional group, the organic compound even having unpaired electrons is made to be more stable.

50 [0028] Since the oxidation-reduction potential is substantially determined depending upon the degree of spread of the unpaired electrons and the symmetry of the orbit, excess spread of the orbit causes an unsatisfactory state to be realized because the oxidation-reduction potential becomes inappropriate. Compounds of the types expressed by the foregoing General Formulas [I] to [V] and formula [VI] having a basic skeleton composed of the benzene ring, which is an aromatic ring having a relatively small molecular weight, are preferred compounds to serve as the redox shuttles in view of the oxidation-reduction potential.

55 [0029] Since the benzene ring, which is the basic skeleton of the foregoing compound, has a molecular weight of

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